

SOME ASPECTS OF THE CALCIFEROUS AMPHIBOLES,  
OXYHORNBLENDE, KAERSUTITE AND  
BARKEVIKITE

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ABSTRACT

The brown calciferous amphiboles oxyhornblende, kaersutite and barkevikite have been examined briefly in terms of their chemistry, optical properties and mode of occurrence. The titaniferous amphibole kaersutite, generally considered to be a variety of oxyhornblende, often has low  $Fe_2O_3/FeO$  ratios and is therefore distinct from the latter mineral. Kaersutite and barkevikite compositions are dominated respectively by the end-member series pargasite-ferropargasite.

Optical properties of brown amphiboles assigned to the three species show considerable overlap. Birefringences greater than 0.040 characterize true oxyhornblendes.

Kaersutite and barkevikite are the brown calciferous amphiboles typically encountered in undersaturated alkaline rocks, barkevikite possessing higher  $Fe^{2+}/Mg$  ratios than kaersutite, and  $Mg < 2$  atoms. Kaersutite occurs most commonly in analcite-bearing rocks of wide compositional range, and in nepheline-bearing basic rocks. On the other hand, barkevikite is more characteristic of the nepheline-syenites, and is an iron-enriched amphibole developed as a consequence of relatively less hydrous conditions resulting in increased  $Fe^{2+}/Mg$  ratios in the magma.

INTRODUCTION

Questions of nomenclature of oxyhornblende\* kaersutite and barkevikite reflect one of the many problems arising from extensive ionic substitution in the calcium-sodium amphibole group. Apart from the problem of identification by optics, actual measurements of optical properties of the three minerals in question are rendered more difficult by their strong brown or reddish-brown absorption colours. And, as emphasized by Boyd (1955), the ways in which the composition of a particular amphibole reflects the chemical and physical environment in which it formed, as yet are not clearly understood.

Amphiboles referred to oxyhornblende, kaersutite and barkevikite have been described from a wide range of igneous rocks. Generally these minerals have been most frequently recognized in alkaline undersaturated types, particularly kaersutite and barkevikite. One feature of their chemistry, namely frequent enrichment in  $TiO_2$ , recalls a similar feature of clinopyroxenes of alkali olivine-basalt magma (Wilkinson, 1956, Table 2). In these minerals,  $TiO_2$  contents of 2-4 per cent are not uncommon.

Basaltic hornblende, oxyhornblende (Winchell, 1932, p. 473) and

\* Throughout this paper the term oxyhornblende is used in preference to the synonymous terms basaltic hornblende and lamprobolite.

lamprobolite (Rogers, 1940) are synonymous terms to cover the dark brown amphibole with high ferric iron content, high indices of refraction and rather strong to extreme birefringence. A small extinction angle also has been cited as a diagnostic optical property. Both Winchell and Rogers have pointed out the unsatisfactory usage of the term basaltic hornblende to cover an amphibole with these properties, as this mineral is by no means confined to basalts.

The term kaersutite was proposed by Lorenzen (1884) for a highly titaniferous amphibole occurring in feldspathic veins and dikes cutting the picrite at Kaersut, Greenland. Lorenzen's original material was subsequently re-examined by Washington and Wright (1908). The term kaersutite has carried various connotations, *e.g.* a highly titaniferous oxyhornblende (Washington and Wright, 1908, p. 210; Benson, 1940, p. 285; Winchell, 1951, p. 437; Kerr, 1959, p. 330); a rare variety of barkevikite (Yagi, 1953, p. 783) and a brown hornblende with abundance of  $\text{TiO}_2$  (Aoki, 1959, p. 278).

Barkevikite (Brögger, 1890) has been variously defined in relation to other amphiboles, *e.g.* as a member of the oxyhornblendes (Kunitz, 1930, p. 214; Sundius, 1946, p. 30) or the soda amphiboles (Winchell, 1951, p. 440).

Attention has been frequently directed to experiments (*e.g.* Kôzu *et al.*, 1927; Barnes, 1930) whereby green hornblende on heat treatment changes to a mineral having the appearance and optical properties of oxyhornblende. In this transformation, the principal chemical change is oxidation of the ferrous iron and loss of hydrogen. Barnes showed that the principal optical changes associated with heating green hornblende in air at about 800° C. are: increase in the indices of refraction, birefringence and dispersion; decrease in the extinction angle and change in 2V to 65°; change in colour and pleochroism from greens to browns.

#### CHEMISTRY AND CLASSIFICATION

In recent years the classification of the calciferous amphiboles has been discussed by Hallimond (1943), Winchell (1945), Sundius (1946), Boyd (1959) and Smith (1959). In general, four principal magnesian end-members (plus their ferriferous analogues) have been recognized (Table 1), namely tremolite (-ferrotremolite or actinolite\*), edenite

\* The terminology of these two ferriferous end-members varies with different authors. In this paper the term ferropargasite is preferred for the pure ferriferous end-member equivalent of pargasite, inasmuch as the term hastingsite for many years has referred to Fe-rich amphiboles with small amounts of MgO, or else to various calciferous amphiboles with variable FeO/MgO ratios (Billings, 1928). The term ferrotremolite is preferred for the Fe-analogue of tremolite.

(-ferroedenite), tschermakite (-ferrotschermakite) and pargasite (-ferropargasite or hastingsite\*). The most significant end-member series in the present discussion is the pargasite-ferropargasite series, the Mg end-member pargasite  $\text{NaCa}_2\text{Mg}_4\text{Al}^{\text{VI}}\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$  being derived from tremolite  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  by the double substitution AlAl for MgSi and NaAl for Si.

Boyd (1959, p. 382) has shown graphically that the two most important end-member series of the calciferous amphiboles (including the more

TABLE 1. END-MEMBERS OF CALCIFEROUS AMPHIBOLES

tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
ferrotremolite	} $\text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
actinolite	
pargasite	$\text{NaCa}_2\text{Mg}_4\text{Al}^{\text{VI}}\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$
ferropargasite	} $\text{NaCa}_2\text{Fe}_4^{2+}\text{Al}^{\text{VI}}\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$
hastingsite	
edenite	$\text{NaCa}_2\text{Mg}_3\text{Al}^{\text{IV}}\text{Si}_7\text{O}_{22}(\text{OH})_2$
ferroedenite	$\text{NaCa}_2\text{Fe}_3^{2+}\text{Al}^{\text{IV}}\text{Si}_7\text{O}_{22}(\text{OH})_2$
tschermakite	$\text{Ca}_2\text{Mg}_3\text{Al}_2^{\text{VI}}\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$
ferrotschermakite	$\text{Ca}_2\text{Fe}_3^{2+}\text{Al}_2^{\text{VI}}\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$

familiar green igneous hornblendes) are  $\text{Ca}_2\text{FM}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  and  $(\text{Na}, \text{K})\text{Ca}_2\text{FM}_4(\text{Al}^{\text{VI}}, \text{Fe}^{3+})\text{Al}_2^{\text{IV}}\text{Si}_6\text{O}_{22}(\text{OH})_2$ , where  $\text{FM} = \text{Fe}^{2+} + \text{Mg}$ . The amphiboles considered by Boyd had  $\text{Ca} = 1.8\text{--}2.1$  and low contents of Ti ( $< 0.20$ ).

Tables 2-4 list analyses of amphiboles assigned by various workers to oxyhornblende, kaersutite and barkevikite respectively. In Table 5, these amphiboles have been recalculated on a basis of 24 (O, OH, F). Much of this latter data has been taken from Hallimond (1943, Table 1). An uncertainty in these calculations is the determination of  $\text{H}_2\text{O}^+$ , and non-determination of F, particularly in older analyses. Only analyses showing reasonably close agreement with the general calcium-sodium amphibole formula  $\text{W}_{2-3}(\text{XY})_5\text{Z}_8\text{O}_{22}(\text{OH})_2^*$  have been listed. Many analyses were rejected because of significant departures of the W (where greater than 3.2) and XY (greater than 5.4) groups.

In the three amphiboles, Si is close to 6 atoms, associated with two Al atoms in four-fold co-ordination. Ca is generally 1.8-2.0. In five cases there is insufficient aluminium to satisfy the  $\text{Al}^{\text{IV}}$  requirements in the

\*  $\text{W} = (\text{Na}, \text{K}, \text{Ca})$ ,  $\text{X} = (\text{Mg}, \text{Fe}^{2+}, \text{Mn})$ ,  $\text{Y} = (\text{Al}^{\text{VI}}, \text{Fe}^{3+}, \text{Ti})$ ,  $\text{Z} = (\text{Si}, \text{Al}^{\text{IV}})$ .

TABLE 2. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF OXYHORNBLÉNDE

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	40.17	39.83	39.85	39.96	42.05	39.82	41.97	39.48	40.69	45.17
TiO <sub>2</sub>	3.78	2.56	4.25	4.05	1.80	2.42	4.20	3.10	2.98	2.11
Al <sub>2</sub> O <sub>3</sub>	15.09	14.98	13.07	12.83	12.50	12.34	12.59	10.97	12.09	7.68
Fe <sub>2</sub> O <sub>3</sub>	5.49	7.66	6.76	7.40	8.61	11.86	4.69	11.23	11.83	14.30
FeO	5.99	3.78	5.09	6.37	6.45	8.02	5.80	8.21	0.21	2.81
MnO	0.09	—	—	—	—	—	n.d.	0.53	0.70	0.41
MgO	12.48	14.44	13.58	12.92	12.40	9.78	14.20	10.30	14.34	13.44
CaO	11.21	12.39	12.42	12.07	12.28	12.26	11.99	13.65	11.85	11.18
Na <sub>2</sub> O	2.27	2.27	2.79	2.28	2.03	2.28	3.17	0.99	2.45	1.35
K <sub>2</sub> O	1.55	1.25	0.98	1.48	0.87	1.03	1.63	0.67	1.56	1.09
H <sub>2</sub> O+	2.10	0.58	0.66	0.72	0.63	0.45	0.26	1.49	1.24	0.10
F <sub>2</sub> O-	0.25	—	—	—	—	—	—	—	—	0.06
etc.	—	—	—	—	—	—	n.d.	0.24	0.10	—
Less O=F	100.47	99.74	99.45	100.08	99.71	100.26	100.50	100.86	100.04	100.14
Total	100.47	99.74	99.45	100.08	99.71	100.26	100.50	100.86	100.04	100.00
α	1.670	1.667	1.677	1.679	1.668	1.681	1.675	—	1.685	1.675
β	1.682	—	—	—	—	—	1.691	—	1.711	1.715
γ	1.693	1.688	1.700	1.701	1.688	1.700	1.701	—	1.731	1.735
γ-α	0.023	0.021	0.023	0.022	0.020	0.019	0.026	—	0.046	0.060
2V <sub>α</sub>	82	—	—	—	—	—	—	—	82	large
γ/Δc	9	3	6	—	—	0	—	—	0-2	5
Pleochroism	Pale yellow with tinge of brown	brownish green	brown	brown	greenish brown	brown	"scarcely noticeable pleochroism"	—	amber yellow	pale yellow
X	dark brown	—	—	—	—	—	—	—	yellowish brown	dark chestnut brown
Y	—	—	—	—	—	—	—	—	reddish brown	dark chestnut brown
Z	dark olive green with tinge of brown	—	—	—	—	—	—	—	—	—
Absorption	X < Y < Z	—	—	—	—	—	—	—	X < Y < Z	X < Y < Z

1. From Iuff-brecchia, L. Balatun, Hungary (Vendl, 1924, p. 238).
2. From tephrite, Grossirieschen, Bohemia (Kunitz, 1930, p. 245).
3. From trachydolerite, Madeira (Kunitz, 1930, p. 245).
4. From volcanic bomb, "Isleta-Krater" (Kunitz, 1930, p. 245).
5. From gabbró, "S. Vincent" (Kunitz, 1930, p. 245).
6. From essexite phonolite, "Tejedatal" (Kunitz, 1930, p. 245).
7. From sodic lava, Kilimanjaro, E. Africa (Washington and Merwin, 1922, p. 124).
8. From hypersthene-andesite, Shabó-zan, Taiwan (Ichimura, 1931, p. 564).
9. From hypersthene-andesite, Shabó-zan, Taiwan (Ichimura, 1931, p. 564). Note: this amphibole referred to brown hornblende by the author. Winchell, 1945, Table 4, treats it as an oxyhornblende.
10. From quartz-lattice, San Juan region, Colorado (Larsen *et al.*, 1937, p. 895. Analysis calculated to 100 per cent from material with 0.79 per cent Fe<sub>2</sub>O<sub>3</sub>).

TABLE 3. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF KAERSUTITE

	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub>	39.30	39.50	40.73	39.51	41.46	40.36	39.78	39.20	39.01	38.30	39.68	40.85
TiO <sub>2</sub>	10.25	11.12	8.47	5.64	5.70	7.09	7.00	6.57	6.05	6.02	7.12	8.47
Al <sub>2</sub> O <sub>3</sub>	11.16	11.12	10.62	14.26	14.24	13.78	14.13	14.87	13.60	12.87	12.81	9.89
Fe <sub>2</sub> O <sub>3</sub>	1.21	0.06	1.39	1.75	3.32	3.39	4.61	4.03	5.25	7.98	4.04	8.85
FeO	8.76	9.44	11.91	10.92	5.70	7.91	7.31	7.33	7.42	6.96	8.79	3.96
MnO	0.06	0.10	0.25	0.09	0.08	0.14	0.12	0.11	0.14	0.12	0.16	0.12
MgO	13.24	12.90	10.46	11.36	13.68	11.08	11.01	11.96	11.73	11.79	11.22	12.47
CaO	11.29	10.91	10.40	10.12	11.62	10.82	10.75	12.37	12.05	10.47	11.06	12.16
Na <sub>2</sub> O	2.93	2.92	2.80	2.80	2.29	2.78	2.57	1.99	2.51	3.11	3.37	2.01
K <sub>2</sub> O	1.06	1.43	1.33	1.59	1.72	1.34	1.58	1.45	1.11	1.30	1.04	0.63
H <sub>2</sub> O <sup>+</sup>	0.59	0.59	1.97	1.68	0.12	0.79	0.37	0.87	0.98	1.10	0.78	0.19
H <sub>2</sub> O <sup>-</sup>	—	—	0.23	nil	—	0.26	0.22	0.27	0.19	0.26	0.15	—
F	0.32	—	—	0.09	0.42	0.37	—	—	0.09	0.05	—	0.10
etc.	—	—	—	—	—	—	—	—	—	—	—	—
Loss O=F	100.17	100.20	100.68	99.81	100.35	100.65	99.45	99.98	100.13	100.33	100.55	99.98
					0.18	0.16				0.02	0.14	0.12
Total	100.17	100.20	100.68	99.81	100.17	100.49	99.45	99.98	100.13	100.31	100.41	99.86
$\alpha$	1.676	—	$\alpha'$ on (110) 1.680	1.677	1.670	1.688	1.687	1.680	1.682	1.684	1.685	1.692
$\beta$	1.694	—	—	1.694	1.692	1.708	1.705	1.700	1.697	1.701	1.710-1.718	1.731
$\gamma$	1.708	—	$\gamma'$ on (110) 1.703	1.707	1.701	1.720	1.718	1.709	1.717	1.720	1.736	1.760
$\gamma-\alpha$	0.032	—	—	0.030	0.031	0.032	0.032	0.029	0.035	0.036	0.051	0.068
$2N_{\alpha}$ meas.	81	—	77-79	82	81	78	80	75	78	—	74-66	71
$2N_{\alpha}$ calc.	82	—	—	81	—	—	79	—	—	—	—	80
$\gamma/\alpha$	8	—	16-19	6	8-10	4	4	—	2	3-5	4	1.5
X	—	—	brownish yellow	pale yellowish brown	light yellow brown	pale yellowish brown	pale yellowish brown	—	pale straw brown	—	pale yellowish brown	pale olivine brown
Y	—	—	reddish brown	brown	reddish brown	brown	reddish brown	—	reddish brown	—	brown	brown
Z	—	—	deep chestnut with violet tinge	dark brown with reddish tinge	brown darker reddish brown	dark brown	reddish brown	—	reddish darker reddish brown	—	deep brown	dark brown
Absorption	—	—	X < Y < Z	X < Y < Z	X < Y < Z	X < Y < Z	X < Y < Z	—	X < Y < Z	—	X < Y < Z	X < Y < Z

1. From vein in picroite, Kaersut, Greenland (Washington and Wright, 1908, p. 198).
2. From picroite, Kaersut, Greenland (Gossner and Spielberger, 1929, p. 121).
3. From monzonite, Morvita district, Satchalin (Yagi, 1953, p. 784).
4. From analcite-basalt, Spring Mount, west of Glen Innes, New South Wales (new analysis).
5. From camptonite, Boulder Dam, Arizona (Cambell and Schenk, 1950, p. 684).
6. From trachyandesite, Gonoura-machi, Iki Islands (Aoki, 1959, p. 279).
7. From kaersutite-basalt dyke (teschenitic), Dago, Oki Islands, Japan (Tomita, 1934, p. 103).
8. From volcanic ejectamenta, Uruyo Island, Korea (Harada, 1936, p. 282).
9. From trachybasalt, Leith Valley Quarry, Dumedin, N. Z. (Benson, 1940, p. 286).
10. From "andesine-basalt," Yohodo, Korea (Kawano, 1937, p. 127).
11. From cognate xenolith in trachyte, Gonoura-machi, Iki Islands (Aoki, 1959, p. 279).
12. From basic lava, Monte Rosso, Linosa (Washington and Wright, 1908, p. 192).

TABLE 4. CHEMICAL ANALYSES AND OPTICAL PROPERTIES OF BARKEVIKITE

	1	2	3	4	5
SiO <sub>2</sub>	38.41	36.12	40.88	41.12	37.86
TiO <sub>2</sub>	1.26	4.82	0.22	0.45	1.25
Al <sub>2</sub> O <sub>3</sub>	16.39	12.46	11.04	11.02	12.06
Fe <sub>2</sub> O <sub>3</sub>	3.75	9.60	7.56	6.54	11.47
FeO	21.75	10.43	17.41	17.73	16.23
MnO	0.15	0.28	1.32	1.03	0.82
MgO	2.54	9.09	5.92	6.14	4.03
CaO	10.52	12.01	10.46	10.42	11.43
Na <sub>2</sub> O	2.95	2.58	3.75	3.65	2.98
K <sub>2</sub> O	1.95	1.41	0.78	0.94	0.72
H <sub>2</sub> O <sup>+</sup>	0.24	1.02	1.16	1.45	1.23
Total	99.91	99.82	100.50	100.49	100.08
$\alpha$	—	1.687	1.691	1.687	1.694
$\beta$	—	—	—	—	—
$\gamma$	—	1.708	1.707	1.701	1.710
$\gamma$ - $\alpha$	—	0.021	0.016	0.014	0.015
2V <sub><math>\alpha</math></sub>	—	—	—	—	—
$\gamma \wedge c$	13	10	16	—	20
Pleochroism					
X	yellow brown	—	—	—	—
Y	dark brown	dark brown	dark brown	greenish brown	brown
Z	dark brown	—	—	—	—
Absorption	X < Y < Z	—	—	—	—

1. From sodalite-syenite, Square Butte, Montana (Lindgren and Melville, 1892, p. 292).
2. From essexite, Fuerteventura, Canary Isles (Kunitz, 1930, p. 245).
3. From nepheline-syenite, Skuttersundskjär (Kunitz, 1930, p. 245).
4. From nepheline-syenite, Stavarnsjö, Norway (Kunitz, 1930, p. 245).
5. From foyaite, S. Vincente, C. Verde (Kunitz, 1930, p. 245).

Z group, and Ti, apparently replacing Si, has been added to bring this group up to 8.00, as required by the amphibole formula. A comparable procedure has been found necessary in certain titaniferous clinopyroxenes.

Several analyses of kaersutite (Table 3, Analyses 1-4) are significant from the point of view of nomenclature inasmuch as they reveal low Fe<sub>2</sub>O<sub>3</sub> contents relative to FeO. The mineral from the type area is included here. This feature of kaersutite chemistry immediately sets it apart from the widely accepted concept of an oxyhornblende. In terms of end members, recalculated analyses of kaersutites with low degrees of oxidation indicate a composition close to that of a titaniferous pargasite with part of the Mg replaced by Fe<sup>2+</sup>. As an approximation, the composition of the type kaersutite can be written as



$(\text{Na, K, Ca})_{2-3}(\text{Mg}_3, \text{Fe}^{2+}) \text{Ti Al}_2^{\text{IV}} \text{Si}_6\text{O}_{23}(\text{OH})$ . In kaersutite the amount of Ti in the Y group is generally between 0.6 and 1. In all cases Mg is greater than 2. Despite variable degrees of oxidation,  $\text{Fe}^{2+}$  is generally greater than  $\text{Fe}^{3+}$ .

The analysis of barkevikite cited by Brögger (1890, p. 412) was incomplete. It is characterised by relatively high lime *and* soda ( $\text{CaO}$  10.24;  $\text{Na}_2\text{O}$  6.08 per cent), making it difficult to place in either the calciferous or alkali amphiboles (Miyashiro, 1957, Table 1). Another analysis of barkevikite from the same area (Table 4, Analysis 3) presents no abnormalities in its composition. Compared with kaersutite, barkevikite is characterised by lower contents of Ti and a higher degree of replacement of Mg by  $\text{Fe}^{2+}$  in the X group, so that  $\text{Fe}^{2+}$  is generally greater than Mg. In the barkevikite analyses, there is a tendency for the W group to closely approach its maximum value of 3.

It is clear that kaersutite and barkevikite compositions are respectively dominated in their compositions by the pargasite-ferropargasite end-members, in which may be particularly noted the replacement of  $\text{Al}^{\text{VI}}$  by both Ti and  $\text{Fe}^{3+}$ .

Billings (1928) proposed the following classification of the hastingsite group based on the ratio  $\text{FeO}/\text{MgO}$  (molecular proportions):  $\text{FeO}/\text{MgO} > 2$ , ferrohastingsite;  $\text{FeO}/\text{MgO} < 2 < 0.5$ , femaghastingsite;  $\text{FeO}/\text{MgO} < 0.5$ , magnesiohastingsite. A classification in this manner possesses limitations when, for any reason, oxidation of the iron has taken place. The brown titaniferous (4–7 per cent  $\text{TiO}_2$ ) amphibole from the Mount Royal essexites (Bancroft and Howard, 1923, p. 20), referred to magnesiohastingsite and femaghastingsite by Billings (*op. cit.*), would be regarded as kaersutites by many workers. Sundius (1946, p. 22) has pointed out the similarity of such Mg-rich amphiboles to pargasite.

It is proposed that the chemical distinction between kaersutite and barkevikite be based on the number of Mg atoms in the formula, titaniferous amphiboles with  $\text{Mg} > 2$  atoms being kaersutites. On this classification the amphibole ( $\text{Mg} = 2.1$ ) from the Fuerteventura essexite (Table 4, Analysis 2) would be referred to kaersutite. Barkevikite is analogous in its fundamental chemistry to the  $\text{TiO}_2$ -poor green or blue-green hastingsites occurring in both acid and over- and undersaturated intermediate rocks.

The term kaersutite has carried with it the implication of a high content of  $\text{TiO}_2$ , generally greater than 5 per cent. This is perhaps unfortunate, as analogous brown amphiboles with 3–5 per cent  $\text{TiO}_2$  are probably not uncommon, particularly in basic alkaline rocks (for example, see Mason, 1958, p. 251). The  $\text{TiO}_2$  content of a particular brown amphibole is sensitive to the magma chemistry at the time of its formation. Viewed



in this light, there appears to be no reason why brown amphiboles conforming in their essential chemistry to kaersutite but possessing slightly lower  $\text{TiO}_2$  contents, should not be covered also by this term. In the writer's opinion, kaersutite should not be regarded as a rare mineral, and it is anticipated that the brown or reddish brown amphibole in intrusive basic alkaline rocks will be of the kaersutite type.

Of those brown amphiboles referred to oxyhornblende, only two (Table 2, Analyses 9 and 10) possess the chemistry and optical properties consistent with oxyhornblende. Of the other amphiboles listed, those types with low birefringences and moderate  $\text{TiO}_2$  contents are more akin to kaersutites with moderate degrees of oxidation. Two amphiboles (Analyses 3 and 5) occur in rocks where there is little possibility of the oxyhornblende reaction having occurred (cf. Hallimond, 1943, p. 70). It may be noted that a graphical representation of selected oxyhornblende compositions (Winchell, 1945, p. 45) indicated a tendency for many compositions to plot closest to a  $\text{Na Ca}_2 (\text{Mg}, \text{Fe}^{2+})_4 (\text{Al}, \text{Fe}^{3+})_3 \text{Si}_6\text{O}_{22} (\text{OH})_2$  end-member.

#### OPTICAL PROPERTIES

The optical properties of analyzed amphiboles referred to oxyhornblende or kaersutite (Tables 2 and 3) suggest that the high birefringences (0.05–0.09) measured on brown amphiboles produced in laboratory heating experiments are not frequently attained in natural material. In particular, the frequency with which the optical properties (particularly  $\gamma - \alpha = 0.068$ ) of the Linosa amphibole (Table 3, Analysis 12) have been quoted, would indicate that such properties have been considered typical of kaersutite. Chemically, the Linosa mineral is atypical when compared with other kaersutites, notably because of its relatively high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratio, a feature which prompted Washington to assign it to a distinct species, *linosite*. It is however akin in its optics and chemistry to an oxyhornblende.

The majority of analyzed kaersutites have ( $\gamma - \alpha$ ) in the range 0.030–0.032. Variation in the  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios apparently has little effect on the birefringence. However a kaersutite with the abnormally high birefringence of 0.083 ( $2V_\alpha = 79-80$ ;  $\text{TiO}_2$  7.55,  $\text{Fe}_2\text{O}_3$  7.11,  $\text{FeO}$  5.05 per cent) has recently been described by Aoki (1959, p. 279). This amphibole occurs as phenocrysts in a scoria. Other kaersutites from the same area with comparable  $\text{TiO}_2$  contents but slightly lower degrees of oxidation possess distinctly lower birefringences (Table 3, Analyses 6 and 11).

Irrespective of the contents of  $\text{TiO}_2$  or total iron, or degree of oxidation of the iron, a large number of kaersutites have  $2V_\alpha = 80 \pm 2^\circ$ .

On the assumption that kaersutite is a titaniferous variety of oxyhorn-

blende, many workers appear to have taken an upper limit of 5 per cent  $\text{TiO}_2$  for oxyhornblende. Despite  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios close to or greater than unity, many amphiboles designated as oxyhornblende have  $(\gamma - \alpha) = 0.019 - 0.026$  (Table 2), particularly those described by Kunitz (1930). These values do not differ markedly from the birefringence of many green hornblendes. Comparison of oxyhornblendes and kaersutites with comparable degrees of oxidation but differing  $\text{TiO}_2$  contents indicates that the birefringence increases slightly with increasing  $\text{TiO}_2$ .

Not a great deal of optical data on barkevikite is available (Table 4). The birefringence is comparable with many of the oxyhornblendes listed in Table 2. With a higher content of  $(\text{FeO} + \text{Fe}_2\text{O}_3)$  and often containing moderate amounts of  $\text{TiO}_2$ , barkevikite might be expected to possess higher refractive indices than kaersutite. There is need for much more data, which may reveal a distinction from kaersutite based on  $2V_\alpha$  (cf. Benson, 1940, p. 289).

It is clear from the data listed in Tables 2-4 that identification of any particular amphibole under discussion cannot be confidently accomplished solely on the over-generalized optical data assigned to these minerals by various workers, since amphiboles referred to these species possess similar ranges of refractive indices, extinction angles and absorption colors. Much more data is necessary in order to define any significance in  $2V$ . The difficulties of optical identification are particularly accentuated by the variation and possible interplay of titania, and degree of iron enrichment and oxidation. The use of low extinction angles as a guide to the degree of oxidation is misleading inasmuch as several kaersutites with low  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios have  $\gamma:c$  values less than 10 degrees. It may also be questioned whether the size of  $2V_\alpha$  is indicative of the degree of oxidation, inasmuch as certain oxyhornblendes with high  $(\gamma - \alpha)$  have  $2V_\alpha \sim 80^\circ$ .

Engel (1959, p. 974) has recently emphasized the lack of obvious correlations of optics and composition of hornblende, particularly in relation to optical properties/composition diagrams. This point is again emphasized, and here attention may be particularly directed to the limitations of optical properties/composition diagrams showing relationships between various amphibole end-members which themselves are titania-free.

The experimental work of Barnes (1930) demonstrated that the increase in the birefringence depends on the iron content of the amphibole, Fe-free or Fe-poor amphiboles showing little or no increase in  $(\gamma - \alpha)$  on heating. Such amphiboles however would be expected to be rare in the normal range of igneous rock compositions. In the formation of an oxyhornblende with comparatively high birefringence, the  $\gamma$  index fre-

quently increases at a greater rate than either the  $\alpha$  or  $\beta$  indices. In view of several natural amphiboles with high degrees of oxidation failing to show strong birefringence, it would seem desirable to investigate carefully the products of controlled heating experiments to determine: (i) Whether differing  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios affect the birefringence. (ii) The nature of the structural changes involved in the production of increased birefringence at known temperatures under controlled oxidizing conditions.

Increased birefringence ( $>0.040$ ) characterizes the oxyhornblendes from Taiwan and Colorado (Table 2, Analyses 9 and 10) and Linosa (Table 3, Analysis 12). These minerals occur in lavas and have high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios. Parsons (1930, p. 31) has listed an amphibole from Bohemia ( $\text{TiO}_2$  5.10,  $\text{Fe}_2\text{O}_3$  6.96,  $\text{FeO}$  2.34 per cent;  $\gamma - \alpha = 0.042$ ) whose chemistry and optics conform to the conventional view of an oxyhornblende. The strongly birefringent amphiboles described by Aoki (1959) appear to represent distinctive types inasmuch as they show comparatively little oxidation. Such amphiboles are worthy of more detailed investigation.

In terms of available analyses and detailed descriptions, it is seen that amphiboles conforming both in chemistry and optical properties (particularly high birefringence) to oxyhornblende, are comparatively uncommon. Pending analysis, it would seem desirable to limit the term oxyhornblende to brown calciferous amphiboles with  $(\gamma - \alpha) > 0.040$  and occurring in lavas. These amphiboles may frequently show strong evidence of magmatic reaction and resorption.

Other brown or reddish-brown amphiboles (particularly those occurring in undersaturated alkaline rocks) with  $(\gamma - \alpha) < 0.040$ , may be conveniently referred to brown hornblendes, unless chemical data results in more precise nomenclature. However, as will be discussed in the occurrence of those minerals, the nature of the parent rock may serve to indicate whether kaersutite or barkevikite is present.

#### OCCURRENCE

Arising from the results of amphibole heating experiments has been the concept that oxyhornblende (and kaersutite) is not strictly a primary mineral, but is an alteration product of common green hornblende (cf. Hatch, Wells and Wells, 1949, p. 66; Winchell, 1951, p. 439), "probably due to hot gases at a late magmatic stage" (Rogers, 1940, p. 828). In the San Juan lavas, Larsen *et al.* (1937, p. 905) considered that "in considerable part the change from common to basaltic hornblende . . . takes place after eruption and during the crystallization of the groundmass." The latter conclusion is substantiated by chemical and optical data on amphiboles within the one volcanic horizon.

If the term oxyhornblende is to carry with it genetic implications, it is clear that this term should not be used indiscriminately to include brown calciferous amphiboles occurring in intrusive rocks (e.g. many kaersutites) and which have been demonstrated to contain low to moderate  $\text{Fe}_2\text{O}_3$  contents. Such amphiboles represent normal magmatic crystallization products.

In the case of brown amphiboles possessing comparatively high  $\text{Fe}_2\text{O}_3$  contents relative to FeO and occurring in intrusive rocks, it is possible that in many cases their composition indicates a response to initially high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios in the parent melts, crystallizing under conditions of high  $[\text{P}]\text{H}_2\text{O}$  or high  $[\text{P}]\text{O}_2$ .

Where brown amphiboles with relatively high  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios, but not possessing abnormal birefringences, are present in lavas, then it is likely that oxidation attendant on extrusion has contributed to their chemistry. In lavas where exothermic surface reactions have resulted in temperatures in excess of  $750\text{--}800^\circ\text{C}$ ., a true oxyhornblende may be locally developed. Those lavas in which a calciferous amphibole is a common ferromagnesian constituent and where there is evidence that such temperatures may be attained (Ingerson, 1955) are represented by andesitic and dacitic types.

Under the appropriate physical conditions it is highly likely that any common calcium-sodium amphibole (including kaersutite and barkevikite) may suffer subsequent conversion to a true oxyhornblende. It may be noted that although some kaersutites occurring as cognate xenocrysts in lavas and dyke rocks (Tomita, 1934; Benson, 1940) show varying degrees of resorption and alteration, nevertheless their degree of oxidation and their birefringence are comparable with similar amphiboles present in intrusives. It is inferred that in such cases oxidation took place at only moderate temperatures.

Kaersutite and barkevikite appear to have been recorded dominantly from undersaturated rocks or those members of a differentiation series, in which the principal undersaturated felsic minerals are respectively analcite and nepheline. The latter amphibole has been most frequently noted in nepheline-syenites.

Although the parent rocks vary in composition from highly basic to intermediate, the range of composition of the kaersutites is not very marked, being mainly restricted to limited replacement in the X group of Mg by  $\text{Fe}^{2+}$ . By contrast, barkevikite reveals a much higher degree of replacement of Mg by  $\text{Fe}^{2+}$ . This feature, together with a tendency for enrichment in Mn with respect to  $\text{Fe}^{2+}$  (cf. Goldschmidt, 1954, p. 628), indicates its precipitation at a relatively advanced stage of differentiation, the magma at that time possessing high  $\text{Fe}^{2+}/\text{Mg}$  ratios. The  $\text{TiO}_2$ -poor amphibole from the Wausau (Wisconsin) quartz-syenite,

referred by Weidman (1907, p. 204) to barkevikite, is associated with fayalite and hedenbergite and is thus a member of an iron-enriched assemblage.

In undersaturated rocks the development of analcite rather than the pair albite-nepheline would be facilitated by high water pressures (cf. Turner and Verhoogen, 1960, p. 124). Such hydrous magmatic conditions would not be favorable to any degree of absolute iron enrichment. Where a calciferous amphibole is precipitated in such an environment, it would be expected to show limited replacement of Mg by  $\text{Fe}^{2+}$  *i.e.* kaersutite would be developed. It is frequently stated that the dark brown amphibole in teschenites is barkevikite, although there appears to be little analytical data to substantiate this claim. It is more likely that the amphibole in question is a kaersutite.

In a nepheline-bearing differentiation series varying in composition from basic to intermediate types, and carrying a brown calciferous amphibole, it is anticipated that a kaersutite would be present in the more basic varieties (*e.g.* the Mount Royal essexites) and that with progressive fractionation, the amphibole would change in its composition towards a barkevikite. Such a trend is analogous to the trend magnesiohastingsite  $\rightarrow$  ferrohastingsite, proposed by Billings (1928, p. 293), and is similar to the trend in hornblendes from certain calc-alkaline igneous series, *e.g.* the amphiboles from the Southern California batholith (Larsen and Draisin, 1950, Table III).

The  $\text{TiO}_2$ -rich environment from which kaersutites have crystallized is illustrated by two examples of co-existing biotites containing 6–8 per cent  $\text{TiO}_2$  (Table 3, Analyses 3 and 4). Some confirmation of the differing magmatic conditions under which kaersutite and barkevikite are precipitated may be furnished by a study with a particular differentiation series of the associated opaque oxides. Unfortunately there appears to be little analytical data on the associated opaques.

In rocks with barkevikite, earlier relatively anhydrous conditions would tend to favor the formation early in the differentiation series of a titanomagnetite composed dominantly of a  $\text{Fe}_3\text{O}_4$ - $\text{Fe}_2\text{TiO}_4$  solid solution and possessing  $(\text{FeO} + \text{TiO}_2) > \text{Fe}_2\text{O}_3$ . In analcite-bearing rocks with kaersutite, the opaque oxides would tend to be either a  $\text{TiO}_2$ -poor magnetite with  $\text{Fe}_2\text{O}_3 > \text{FeO}$ , or else a magnetite of the  $\text{Fe}_3\text{O}_4$ - $\text{FeTiO}_3$  solid solution type. Concentration of  $\text{TiO}_2$  at the stage of kaersutite precipitation would be facilitated by the early separation of a  $\text{TiO}_2$ -poor magnetite.

Ultimate clarification of many of the proposals in the present discussion obviously must await more detailed studies on possible chemistry/optical properties relationships and response by the amphibole chemistry

to varying conditions of differentiation. In particular, a great deal remains to be done concerning the effects of dominant cations (particularly Ti) on optics; in addition, x-ray diffraction studies represent a field where considerable information is needed.

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## REFERENCES

- AOKI, K. (1959), Petrology of alkali rocks of the Iki Islands and Higashi-matsura District, Japan: *Sci. Rept. Tohoku Univ.*, **6**, Ser. III, 261-310.
- BANCROFT, J. A. AND HOWARD, W. V. (1923), The essexites of Mount Royal, Montreal: *Trans. Roy. Soc. Canada*, **17**, 13-43.
- BARNES, V. E. (1930), Changes in hornblende at about 800° C.: *Am. Mineral.*, **15**, 393-417.
- BENSON, W. N. (1940), Kaersutite and other brown amphiboles in the Cainozoic igneous rocks of the Dunedin district: *Trans. Roy. Soc. N.Z.*, **69**, 283-308.
- BILLINGS, M. P. (1928), The chemistry, optics and genesis of the hastingsite group of amphiboles: *Am. Mineral.*, **13**, 287-296.
- BOYD, F. R. (1955), *Ann. Rept. Geophys. Lab. Washington for 1954-55*, 115-119.
- BOYD, F. R. (1959), *Researches in Geochemistry*, ed. P. H. Abelson, 377-396: John Wiley and Sons, N. Y.
- BRÖGGER, W. C. (1890), Die Mineralien der Syenitpegmatitgänge der sudnorwegischen Augite- und Nephelinsyenite: *Zeits. Kryst.*, **16**, 412-418.
- CAMPBELL, I. AND SCHENK, E. T. (1950), Camptonite dykes near Boulder Dam, Arizona: *Am. Mineral.*, **35**, 671-692.
- ENGEL, C. G. (1959), Igneous rocks and constituent hornblendes of the Henry Mountains, Utah: *Geol. Soc. Amer. Bull.*, **70**, 951-980.
- GOLDSCHMIDT, V. M. (1954), *Geochemistry*: Clarendon Press, Oxford, 730 pp.
- GOSSNER, B. AND SPIELBERGER, F. (1929), Chemische und röntgenographische Untersuchungen an Silikaten: *Zeits. Kryst.* **72**, 111-142.
- HALLIMOND, A. F. (1943), On the graphical representation of the calciferous amphiboles: *Am. Mineral.*, **28**, 65-89.
- HARADA, Z. (1936), Chemische Analysenresultate von Japanischen Mineralien: *J. Fac. Sci. Hokkaido Imp. Univ.*, **3**, Ser. 4, 221-362.
- HATCH, F. H., WELLS, A. K. AND WELLS, M. K. (1949), *The Petrology of the Igneous Rocks*: Thos. Murby and Sons, London, 469 pp.
- ICHIMURA, T. (1931), Notes on brown hornblende and biotite from Shabō-zan, of the Daiton Volcanoes, Taiwan: *Mineral. Mag.*, **22**, 561-568.
- INGERSON, E. (1955), Methods and problems of geologic thermometry: *Econ. Geol.*, **50th Ann. Vol.**, 341-410.
- KAWANO, T. (1934), Chemical formula of basaltic hornblende: *Proc. Imp. Acad. Jap.*, **10**, 349-352.
- KERR, P. F. (1959), *Optical Mineralogy*, 3rd Ed.: McGraw-Hill Book Co., N. Y., 442 pp.
- KŌZU, S., YOSHIKI, B. AND KANI, K. (1927), Note on the transformation of common hornblende into basaltic hornblende at 750°C.: *Sci. Rept. Tōhoku Imp. Univ.*, **3**, Ser. III 143-159.

- KUNITZ, W. (1930), Die Isomorphieverhältnisse in der Hornblendegruppe: *Neues Jahrb. Mineral.*, **60**, Abt. A, 171-250.
- LARSEN, E. S. *et al.* (1937), Petrologic results of a study of the minerals from the Tertiary volcanic rocks of the San Juan region, Colorado: *Am. Mineral.*, **22**, 889-905.
- LARSEN, E. S. AND DRAISEN, W. M. (1950), Composition of the minerals in rocks of the Southern California batholith: *Rept. 18th Int. Geol. Cong.*, Pt. II, 66-79.
- LINDGREN, W. AND MELVILLE, W. H. (1892), A sodalite-syenite and other rocks from Montana: *Am. J. Sci.*, Ser. 3, **45**, 286-297.
- LORENZEN, J. (1884), *Medd. Grønland*, **7**, 27.
- MASON, B. (1958), The intrusive rocks of the Kaikoura Mountains, Marlborough, New Zealand: *Trans. Roy. Soc. N.Z.*, **85**, 247-262.
- MIYASHIRO, A. (1957), The chemistry, optics and genesis of the alkali amphiboles: *J. Fac. Sci. Tokyo Univ.*, **11**, Sect. II, 57-83.
- PARSONS, A. L. (1930), A chemical and optical study of amphibole: *Univ. of Toronto, Geol. Ser. No. 29*, 29-33.
- ROGERS, A. F. (1940), Lamprobolite, a new name for basaltic hornblende: *Am. Mineral.*, **25**, 826-828.
- SMITH, J. V. (1959), Graphical representation of amphibole compositions: *Am. Mineral.*, **44**, 437-440.
- SUNDIUS, N. (1946), The classification of the hornblendes and the solid solution relations in the amphibole group: *Sverig. Geol. Unders. (Årsbok)*, **40**, No. 4, 1-36.
- TOMITA, T. (1934), On kaersutite from Dôgo, Oki Islands, Japan, and its magmatic alteration and absorption: *J. Shanghai Sci. Inst.*, Sect. 2, **1**, 99-136.
- TURNER, F. J. AND VERHOOGEN, J. (1960), *Igneous and Metamorphic Petrology*, 2nd Ed.: McGraw-Hill Book Co. Inc., N. Y., 694 pp.
- VENDL, M. (1924), The chemical composition and optical properties of a basaltic hornblende from Hungary: *Mineral. Mag.*, **20**, 227-240.
- WASHINGTON, H. S. AND WRIGHT, F. E. (1908), On kaersutite from Linosa and Greenland: *Am. J. Sci.*, **26**, 187-211.
- WASHINGTON, H. S. AND MERWIN, H. E. (1922), Augite and hornblende from Kilimanjaro: *Am. Mineral.*, **7**, 121-125.
- WEIDMAN, S. (1907), The geology of north central Wisconsin: *Wisc. Geol. Surv. Bull.* **16**, 697 pp.
- WILKINSON, J. F. G. (1956), Clinopyroxenes of alkali olivine-basalt magma: *Am. Mineral.*, **41**, 724-743.
- WINCHELL, A. N. (1932), Ferrotremolite, oxyhornblende and tourmaline: *Am. Mineral.*, **17**, 472-477.
- WINCHELL, A. N. (1945), Variations in composition and properties of the calciferous amphiboles: *Am. Mineral.*, **30**, 27-50.
- WINCHELL, A. N. (1951), *Elements of Optical Mineralogy*, Part II: John Wiley and Sons, N. Y., 551 pp.
- YAGI, K. (1953), Petrochemical studies on the alkalic rocks of the Morotu district, Sakhalin: *Geol. Soc. Amer. Bull.*, **64**, 769-810.

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